ON THE APPLICABILITY OF STEPANOV'S RELATION IN THE CASE OF VISCOUS, QUENCHED SOLUTIONS

By J. HEVESI and L. KOZMA

Institute of Experimental Physics, The University, Szeged

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It has been studied how STEPANOV's relation is fulfilled in the case of viscous, quenched solutions. The results show that the relation can be employed in the case of different concentrations of the quencher as well as of different viscosities. The considerable variability of T^* with the viscosity has been qualitatively interpreted.

1. STEPANOV found the relation

$$\frac{f_e(\nu)}{k(\nu)} = d(T)\,\nu^3 e^{-\frac{h\nu}{kT}} \tag{1}$$

describing the connection between absorption and fluorescence spectra of complicated molecules on the basis of theoretical considerations [1], but the conditions in which eq. (1) is fulfilled are not sufficiently determined by the assumptions. By using new assumptions KETSKEMÉTY and co-workers [2], came to the formula

$$\frac{f_e(\nu)}{k(\nu)} = d(T)\eta^*(\nu)\,\nu^3 e^{-\frac{h\nu}{kT}} n^2(\nu) \tag{2}$$

the applicability of which is better determined by the new suppositions. In these relations $f_e(\nu)$ means the fluorescence, $k(\nu)$ the absorption spectra; $d(T)$ is a constant independent of ν, h and k are Planck's and Boltzmann's constants, T the temperature of the solution. Owing to the yield function (1) and (2) differ considerably within certain spectral regions, whereas in other regions they are in good agreement.

If eq. (1) is fulfilled, the function

$$F(\nu) \equiv 3\ ln\ \nu - ln f_e(\nu) + ln\ k(\nu) \tag{3}$$

plotted *versus* ν gives a straight line. The temperature T can be determined from the slope of the straight. Already the first experiments led to the surprising result, that the temperatures calculated in this way (subsequently denoted T^*) are generally higher than the true temperatures T of the solutions. This statement has been confirmed by later calculations.

ALENCEV [3] interpreted the fact, that $T^* \geqq T$ by supposing that part of the energy absorbed by the molecules is transformed into vibrational energy and if the transfer of this energy to the solvent does not take place in a considerably shorter time than τ, the mean life time of the excited states, then the excited molecule will

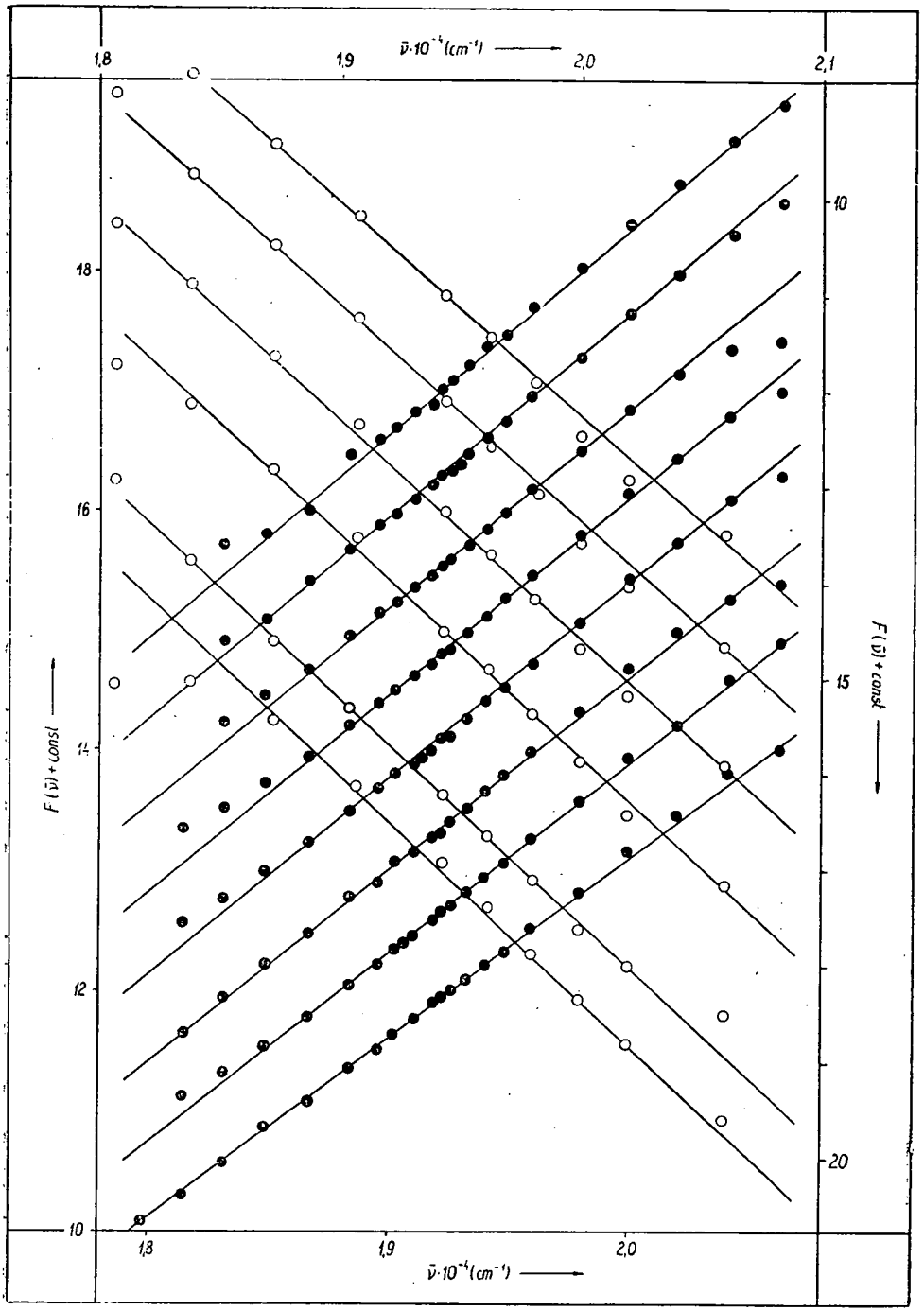

Fig. 1. a) Straights calculated with solutions of constant glycerine concentrations (o o o)
b) Straights calculated with solutions of constant quencher concentrations (● ● ●)

remain in the „heated" state. Other authors saw the cause of this phenomenon in the changes of the absorption spectra caused by the absorbing foreign (non fluorescing) substances contained by the solutions [4], [5].

It can be seen that if T^* is not only apparently higher than T, then the difference of the temperatures $\Delta T = T^* - T$ must be in a close connection with the physical characteristics of the solution, *e. g.* mean life time of the excited states (depending on the degree of quenching), viscosity of the solutions and wavelength of the exciting light. The aim of our investigations was to study the dependence of ΔT on the abovementioned characteristics.

2. The measurements were carried out by using eq. (1), taking care to calculate T^* from data belong ing to frequency regions in which eq. (1) and (2) are in good agreement.[1]

The first part of our studies was carried out on a group of fluorescein solutions with constant concentrations of fluorescein, glycerin and NaOH ($1 \cdot 10^{-4}$ mol/l, 60 vol. %, and 3 weight % respectively) the concentration c_{KJ} of the quencher (KJ) varying between 0—1 mol/1. The spectra are published in a former paper [7]. The functions $F(\nu)$ calculated from these spectra are plotted in Fig. 1. As the figure shows, in the case of these solutions the linear relations were fulfilled as expected.

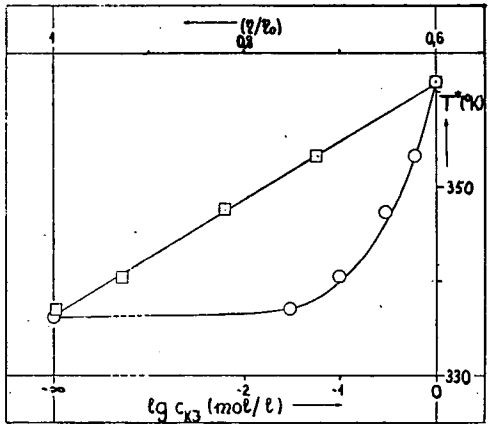

Fig. 2. Values of T^* *versus* $\lg c_{KJ}$ (o o o) and η/η_0 (□ □ □)

In Fig. 2 the temperatures T^* calculated from the slope of the straight lines of Fig. 1 are plotted *versus* $\lg c_{KJ}$ and the relative yield η/η_0 of the solutions measured with the method given in [8]. The figure shows that T^* increases with increasing c_{KJ}. It can be similarly seen that the increase of T^* with the decrease of η/η_0 is linear. Important data of these solutions are given in Table I.

Table I.

η_v, T^* and η in solutions of different KJ concentrations

KJ (mol/1)	0	$3 \cdot 10^{-2}$	$1 \cdot 10^{-1}$	$3 \cdot 10^{-1}$	$6 \cdot 10^{-1}$	1
η_v (cP)	28,016	28,542	28,690	29,226	30,351	32,532
T^* (°K)	336,11	336,98	340,4	347,3	353,18	361,68
η	0,94	0,93	0,90	0,78	0,39	0,22

[1] In the case of glycerine solutions GALANIN's [6] experimental data were taken as basis for the form of the function $\eta^*(\nu)$; as GALANIN paper shows, the yield function $\eta^*(\nu)$ of glycerinous fluorescein solutions can be regarded as constant from 495 mμ to 515 mμ with an error of ± 2,5%. Data involved in our calculations are taken from this spectral region.

The second part of our work involved a series of solutions with constant concentrations of fluorescein, NaOH and quencher (KJ) — $1 \cdot 10^{-4}$ mol/l, 3 weight %, and $3 \cdot 10^{-1}$ mol/l respectively — and glycerine concentrations varying from 0 to 85 vol. %. The absolute yield η was measured with the method given in [9]. In Fig. 3 η is plotted *versus* glycerine concentration. It can be seen that the yield η increases with the glycerine concentration (*i. e.* with the viscosity η_v) as described by several authors (see *e. g.* [10]). Fig. 4 shows the absorption spectra, Fig. 5 the fluorescence spectra, the latter in arbitrary units. It can be seen that with the increase of the glycerine concentration the maxima of both spectra are shifted toward the longer waves (according to the experiences of other authors; see *e. g.* [11]). The spectra were measured with a grating spectrophotometer Optica Milano, Type CF-4, and the true fluorescence spectra determined using the method desribed in [9]. The straight lines calculated with eq. (3) are also plotted in Fig. 1. As in the case of the solutions of the first group, the agreement with eq. (1) is good. (It is to be noted that in our calculations quantum spectra are used and eq. (3) is written correspondingly).

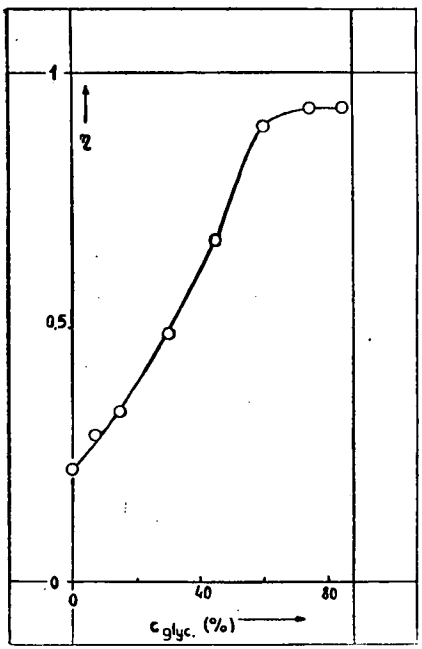

Fig. 3. Absolute yield η *versus* glycerine concentration in vol. %.

Table II. gives the glycerine concentrations of the solutions in vol. %, the viscosity η_v (measured with a Höppler-viscosimeter), the absolute yield η and the values of T^* calculated from eq. (3). Fig. 6 shows the values of T^* *versus* η_v respectively η/η_{max}.

Table II.

η_v, T^* and η in solutions of different glycerine concentrations

Glic. konc. %	0	7,5	15	30	45	60	75	85
η_v (cP)	1,10	1,48	1,81	3,66	8,10	21,4	77,51	421,03
T^* (°K)	294,9	299,2	300,6	303,5	305,0	309,5	312,6	330,8
η	0,218	0,285	0,383	0,488	0,672	0,897	0,930	0,930

The comparison between the T^* shown in Fig. 2 — measured with constant concentration of fluorescein, NaOH and glycerin and variable concentration of the quencher — and the T^* shown in Fig. 6 — measured in solutions of constant fluorescein, NaOH and KJ concentration and varying glycerine concentrations — leads to the following important statements:

a) The values of T^* of the second group, calculated with solutions of variable

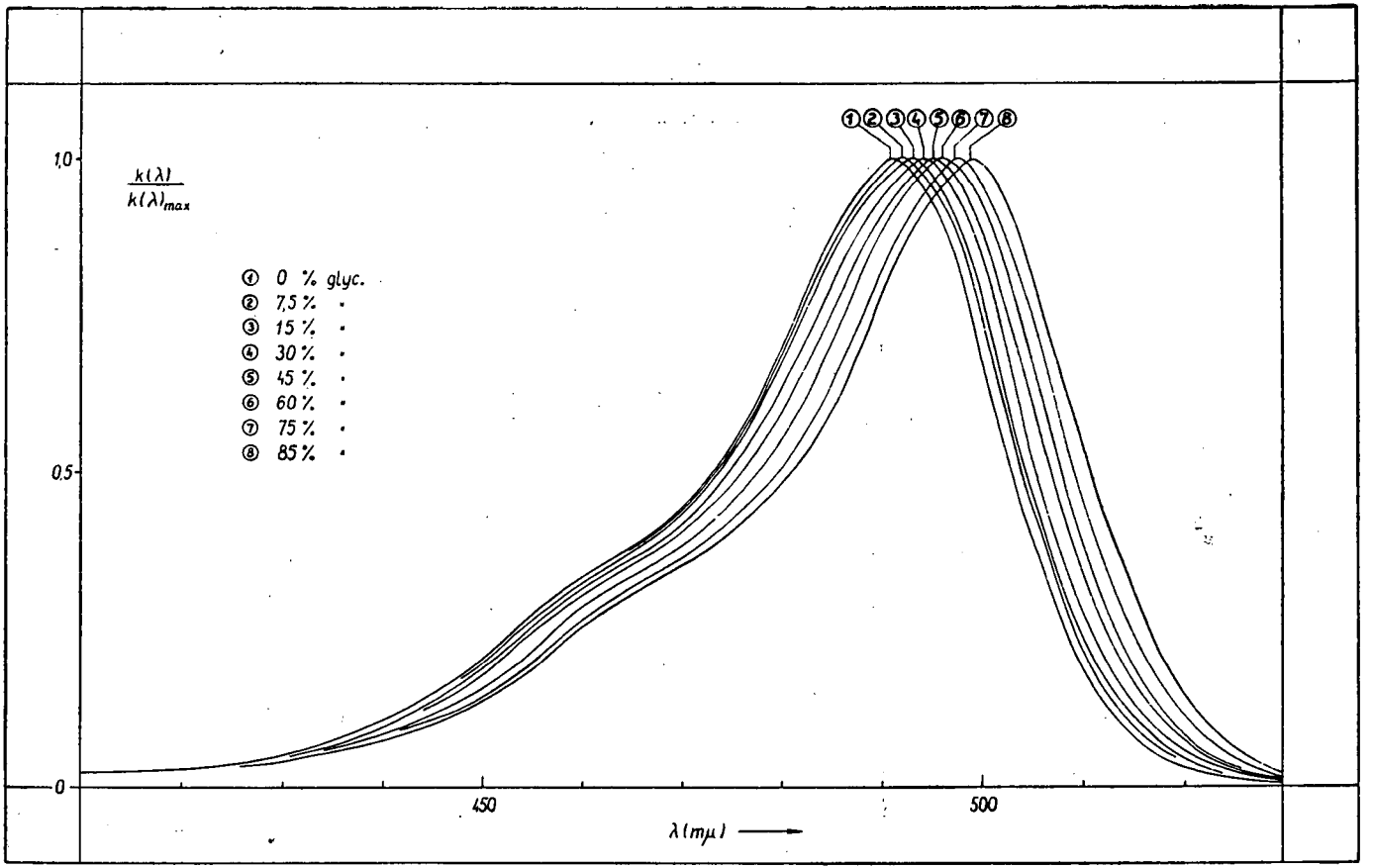

Fig. 4. Absorption spectra of solutions of different glycerine concentration

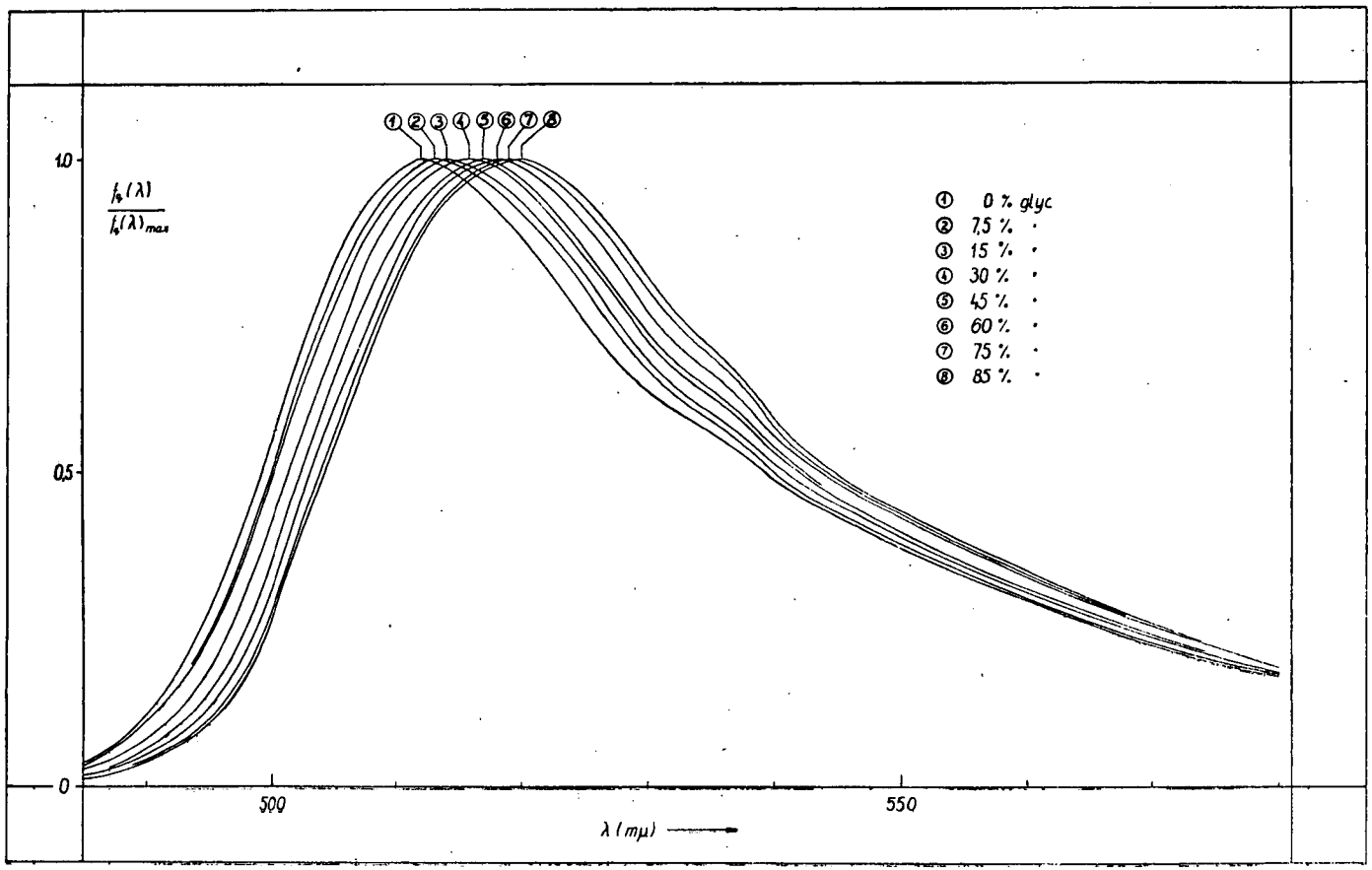

Fig. 5. Fluorescence spectra of solutions of different glycerine concentration

glycerin concentrations, are substantially lower (with aqueous solution equal to the room temperature), then those of the first group, calculated with solutions of varying concentration of the quencher.

b) In the second group T^* increases with increasing η/η_{max} (more than linearly), whereas in the case of the first group it was found to decrease linearly.

3. The increase of T^* with the concentration of the quencher is in accordance with the quenching mechanism. The higher concentration of the quencher reduces the mean life time of the excited state [10], therefore the absorbed energy can not be totally emitted and will serve partly to produce the temperature $T^* > T$. It is easy to understand that this „remaining energy" — viscosity and temperature beeing the same — depends essentially on the mean life time of the excited state, that is on the concentration of the quencher.

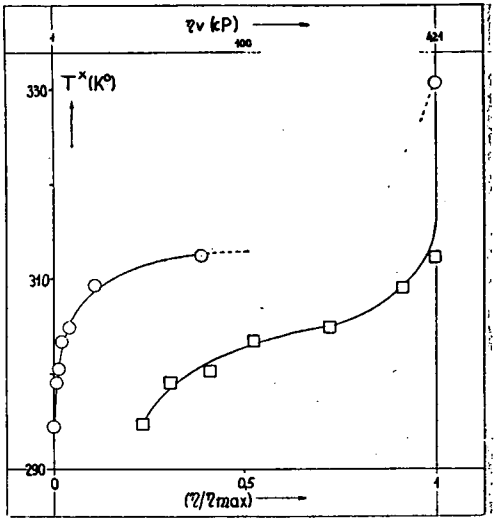

Fig. 6. Values of T^* *versus* η_v (o o o) and η/η_{max} (□ □ □)

The increase of T^* with the viscosity measured with constant concentration of the quencher (see Fig. 6) can be probably interpreted by the shift of the absorption and fluorescence spectra toward the longer waves. It has been shown in [2] that in some cases T^* increases with diminishing wavelengths of the exciting light. In our case the wavelength of exciting light was constant but the mean wavelengths shifted toward the longer waves with increasing viscosity. Essentially the differences of the exciting and the emitted energy increased both in the case examined by [2] and in the case our investigations and this resulted in the increase of T^* in both cases. In order to clear up the problem more exactly, it would be of interest to study in detail the dependence of T^* on the wavelengths of the exciting light and on the shift of the absorption and the fluorescence spectra. Investigations to this purpose are in course.

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О ПРИМЕНИМОСТИ СООТНОШЕНИЯ СТЕПАНОВА В СЛУЧАЕ ВЯЗКИХ, ПОТУШЕННЫХ РАСТВОРОВ

Я. Хевеши и *Л. Козма*

В работе исследовалось выполнение соотношения *Степанова* для вязких, потушенных растворов. Результаты показывают, что так в случае различного тушения, так и различной вязкости можно применять соотношение *Степанова*. Мощное изменение T^* с вязкостью получило качественное истолкование.